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I, KAY WARD, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PP 6275 for a patent by ADVANCED PROJECT GROUP PTY. LTD. filed on 01 October 1998.

WITNESS my hand this
Sixteenth day of November 1999

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Regulation 3.2

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A U S T R A L I A

Patents Act 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"Method for Treatment of Vulcanized Rubber"

The invention is described in the following statement:

METHOD FOR TREATMENT OF VULCANIZED RUBBER

The present invention relates to a method for the treatment of vulcanized rubber, in particular waste rubber, and a chemical solution for use in such a treatment method. In particular, the invention relates to a method for reclaiming waste rubber such as rubber crumb from used tyres, tyre tubing, hosing or other scrap, by devulcanization.

Sulfur vulcanization of a rubber polymer is a chemical process which forms a three dimensional network by interconnecting polymer chains, such as through sulfur atoms. Various other vulcanization systems are also possible including processes where the cross-linking entity is a carbon-carbon bond, a divalent organic radical, or a polyvalent metal. These processes produce vulcanized rubber having increased elasticity and decreased plasticity. In this regard, vulcanized rubber generally retracts forcibly to its moulded shape after being deformed by some type of mechanical force.

The ever increasing cost of crude natural rubber, primarily due to its scarcity, has made the recycling or reclaiming of waste rubber economically attractive for many years. For example, several acid processes for reclaiming rubber are known. Such processes are typically applicable to the treatment of waste rubber having a relatively low state of vulcanization and containing no free sulfur. These processes are, however, generally not suitable for more highly vulcanized rubber such as hose, belting and tyre scrap. Furthermore, rubber which has been reclaimed by acid processes usually disadvantageously contains small traces of acid which cause rapid deterioration of the rubber. The tensile strength and other physical properties of acid reclaimed rubber are generally poor.

Alkali processes for reclaiming rubber are also known, and are generally considered to provide some advantages over the above mentioned acid processes. However, sulfur contained in the waste rubber is not removed by alkali processes, but rather the bonding between the sulfur and the rubber is altered. Disadvantageously, after scrap vulcanized

rubber has been reclaimed through an alkali process, it typically loses toughness and elasticity, and generally becomes susceptible to plastic deformation.

According to the present invention there is provided a method for the treatment of vulcanized rubber comprising the steps of:

providing a solution of sulfur in a fatty acid or ester or a salt thereof;

blending the solution with particulate vulcanized rubber; and

heating the blend for a time period and at a sufficient temperature and pressure to substantially devulcanize the rubber.

Preferably an oil-base softening agent is added to the blend prior to heating of the blend to soften the rubber during treatment. The addition of softening agent is particularly preferred if the rubber being treated is dry. On the other hand, if the rubber is relatively fresh scrap, the softening agent may not be required. An appropriate amount of softening agent may generally be determined empirically from the nature of the rubber.

During blending of the vulcanized rubber with the solution and optionally the softening agent, it is preferred that the mixing vessel be cooled, for example by water cooling. Cooling of the blend advantageously ensures that the blend does not become sticky and, therefore, unable to be thoroughly blended.

The blend may be heated for any suitable time period depending on, for example, the degree of vulcanization of the rubber being treated and/or the particle size of the particulate rubber. However, the blend is typically heated for a time period of from about 1 hour to about 8 hours, preferably from about 4 to about 8 hours.

The temperature at which the blend is heated is advantageously chosen to avoid burning of the rubber being treated. In this regard, the blend is preferably heated at a temperature of from about 180°C to about 200°C. Similarly, the pressure at which the treatment is conducted may be determined based on the degree of vulcanization of the rubber and

depending on the selected time period and temperature of treatment. In a preferred embodiment, the treatment is carried out at a pressure of from about 18 to about 20 kg/cm^2.

The amounts of the constituents of the blend will generally depend on the particular characteristics of the rubber to be treated. For example, the amount of solution of sulfur and fatty acid or ester or salt thereof may vary depending on the degree of vulcanization of the rubber. In a preferred embodiment the blend comprise about 100 parts particulate rubber, 4 to 6 parts softening agent and 2 to 4 parts treatment solution.

The particulate rubber may be of any suitable particle size. Generally, the smaller the particle size the more effective and efficient the reaction. In a preferred embodiment the rubber is rubber crumb having a particle size of less than 6mm. Most preferably the rubber is powdered rubber.

The solution of sulfur and fatty acid or ester or salt thereof preferably comprises a solution of sulfur and fatty acid or ester or salt thereof in a ratio of 1:4. However, the concentration of sulfur in the solution may vary depending on the degree of vulcanization of the rubber. In a preferred embodiment, the fatty acid or ester or salt thereof is an unsaturated fatty acid or ester or salt thereof. More preferably the fatty acid is oleic acid.

The solution is preferably prepared by adding powdered ventilated sulfur to oleic acid which has been heated to approximately to 160°C while stirring the solution. After the addition of the sulfur, typically in a ratio of sulfur to oleic acid of 1:4, the temperature of the solution is increased until the sulfur is completely dissolved in the oleic acid. Generally, it has been found that a temperature of 180°C is sufficient to dissolve the sulfur in the oleic acid. Alternatively, the sulfur may be added to cold oleic acid, and the solution subsequently heated to dissolve the sulfur.

Accordingly, the invention also provides a solution for treating a vulcanized rubber, the solution comprising:

a fatty acid or ester or a salt thereof; and

sulfur.

The oil based softening agent may comprise any suitable softening agent. However, in a preferred embodiment the softening agent is an aromatic oil. For example, in some embodiments a filtered sump oil may be used as the oil based softening agent.

The heating of the blend may be achieved by any suitable means. In a preferred embodiment however, heating is achieved in an autoclave, most preferably a rotating autoclave. Rotation facilitates an even heating of the blend being treated. For example, a "Maxiterm" autoclave has been found appropriate for this purpose. Alternatively, it is envisaged that the entire process or at least a substantial part of the process, may be achieved using a continuous process. In this regard, the treatment process may comprise conveying the material to be treated through a number of treatment stages, each of which carries out a step in the process of the invention.

When heating is conducted in an autoclave the blend is preferably placed in trays having a depth of approximately 10cm. The blend is preferably evenly spread in the tray to a depth of approximately 5cm.

Following heating the blend is cooled or allowed to cool. For example, cooling may be effected using a water cooling system. Once the blend is cooled, it is transferred to a milling station where it is milled, again preferably with water cooling. Most preferably the treated rubber is milled a plurality of times, for example three times.

The milled rubber is preferably then heated, for example in an oven, up to about 130°C. Following heating, the rubber is once again cooled and remilled. The remilled rubber, which is substantially 100% reclaimed rubber, may then be formed into pallets for sale.

Advantageously, waste rubber treated by the method according to the invention produces

reclaimed rubber which may be similar to crude rubber, and can advantageously be used in the manufacture of rubber articles. Also, the reclaimed rubber may be revulcanized in the normal manner, or it may be mixed with synthetic rubber or natural rubber as required.

Preferred embodiments of the present invention will now be described in more detail with reference to the following examples which should not be construed as limiting on the invention in any way.

Preparation of sulfur solution

1000g of oleic acid was introduced to a cold reactor and 250g of powered ventilated sulfur was added thereto with stirring. The reactor was closed with continual mixing of the solution. The solution was then heated to between 160°C and 180°C to completely dissolve the sulfur in the oleic acid. The solution is then allowed to cool.

Throughout the heating process, the solution was periodically checked to see whether the sulfur had dissolved. Generally, the solution was checked at about 150°C, 160°C and 170°C by placing a drop of the liquid on a glass plate. If the drop was not clear, the sulfur was not completely dissolved. Heating was continued until a clear and transparent drop was achieved on the glass plate.

Care should be taken when preparing the sulfur solution to evacuate or eliminate any sulfur dioxide gas produced. This may be achieved through an exhaust fan or by using a caustic vapour trap.

Treatment of waste rubber

1. Rubber Devulcanization Process

Car tyre crumb rubber particles and chemical additives were weighed to the specified

formulation. The ingredients were well mixed in a rotational mixer. The blend was then placed in layers in a device and heated. The resulting product was then milled on a two roll mill.

For truck tyre crumb rubber particles, the same procedure was followed.

2. Preparation of Rubber Samples

The treated rubber was mixed with curatives at three levels, viz

Car tyre sample:

(d) 50% devulcanized rubber and 50% virgin uncured tyre tread (mainly natural rubber).

(e) 60% devulcanized rubber and 40% virgin uncured tyre tread.

(f) 30% devulcanized rubber and 70% virgin uncured tyre tread.

Truck tyre sample:

(g) 50% treated rubber and 50% virgin uncured tyre tread (mainly natural rubber).

(h) 60% treated rubber and 40% virgin uncured tyre tread.

(i) 30% treated rubber and 70% virgin uncured tyre tread.

The above car and truck tyre samples were processed on a two roll mill and there were no processing difficulties encountered. The treated rubber blended with the virgin tyre stock without difficulties.

The samples were cured under normal curing conditions for truck tyres in a compression press.

3. Sample Evaluation

3.1 Specimen Preparation and Conditioning

Test specimens were cut to ASTM D412 Die C from cured samples (d), (e), (f), (g), (h), (i) and conditioned at 23°C, 50% humidity for 24 hours.

3.2 Testing Conditions

Testing machine: LLOYD 2000R with computer interface;

Testing speed: 500 mm/min

Temperature: 23°C

Humidity: 50%

Specimens tested: 3 for each sample

3.3 Test Results

The average results are summarised in the following table.

Car Tyre

Sample I.D. (Devulcanized rubber/tyre tread stock)	Tensile Strength (Mpa)	Modulus (Mpa) at 300% Elongation	Elongation at Break (%)	Hardness (Shore A)
(d) (50/50)	4.29	2.57	463.6	56.8
(e) (60/40)	4.74	2.76	489.7	56.4
(f) (30/70)	7.23	2.61	702.4	58.0

Truck Tyre

Sample I.D. (Devulcanized rubber/tyre tread stock)	Tensile Strength (Mpa)	Modulus (Mpa) at 300% Elongation	Elongation at Break (%)	Hardness (Shore A)
(g) (50/50)	6.5	3.0	559.4	59
(h) (60/40)	7.2	3.3	586.1	58
(i) (30/70)	9.8	2.7	803.3	61

Conclusion

The rubber devulcanization process is capable of producing a product that is compatible with rubber compounds. The performance of these compounds can be optimised with regard to the cure system, polymer type, filler level, sulfur level and level of addition of the devulcanized material.

The tests conducted within our laboratories show that including 30% of devulcanized material derived from passenger tyres into a tread formulation has resulted in a material with useful properties, i.e. significant tensile strength, modulus, elongation and hardness.

These values can be further improved by adjustments to the formulation. The product properties would depend on the actual formulation being cured and the curing conditions.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

DATED this FIRST day of OCTOBER, 1998.

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